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(54) [Title of the Invention] Rubber Composition for Tire Bead Filler

(57) [Abstract]

[Problem]

To provide a rubber composition that is useful as a rubber material arranged to the bead part of the tire, particularly a rubber composition that is useful as a bead filler with increased elastic modulus without damage to its fatigue resistance.

[Means for Resolution]

A rubber composition for tire bead filler, which comprises from 3 to 20 parts by weight of silica and from 0.5 to 3 parts by weight of resorcin or a resorcin derivative, based on 100 parts by weight of a rubber component comprising from 10 to 40% by weight of a cis-1,4-bonded polybutadiene rubber modified with a syndiotactic-1,2-bonded polybutadiene and from 90 to 60% by weight of a diene-based rubber other than the cis-1,4-bonded polybutadiene rubber modified with a syndiotactic-1,2-bonded polybutadiene, wherein hexamethylenetetramine or a melamine derivative is further contained in an amount of from 0.8 to 2.0 times by weight of the blending amount of the resorcin or resorcin derivative, and storage elastic modulus (E') of its vulcanizate at a temperature of 30°C is from 8 to 15 MPa.

[Claim]

[Claim 1]

A rubber composition for tire bead filler, which comprises from 3 to 20 parts by weight of silica and from 0.5 to 3 parts by weight of resorcin or a resorcin derivative, based on 100 parts by weight of a rubber component comprising from 10 to 40% by weight of a cis-1,4-bonded polybutadiene rubber modified with a syndiotactic-1,2-bonded polybutadiene and from 90 to 60% by weight of a diene-based rubber other than the cis-1,4-bonded polybutadiene rubber modified with a syndiotactic-1,2-bonded polybutadiene, wherein hexamethylenetetramine or a melamine derivative is further contained in an amount of from 0.8 to 2.0 times by weight of the blending amount of the resorcin or resorcin derivative, and storage elastic modulus (E') of its vulcanizate at a temperature of 30°C is from 8 to 15 MPa.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

This invention relates to a rubber composition for use in the rubber members having high elastic modulus to be arranged in the bead part, particularly bead filler.

[0002]

[Related Art]

In general, in order to effectively provide a tire with the force generated from its rim which changes traveling direction of the tire when the steering wheel is turned, each tire is designed in such a manner that a large stress is generated in its carcass by increasing rigidity of the bead part. Accordingly, a rubber composition having high elastic modulus is also used in the formation of bead filler for filling the wind up part which is formed when edge part of the carcass ply is fastened by bending from inside toward outside along the bead core and the space encircled by the carcass ply body part

and bead core. Mostly used in the bead filler include a rubber composition in which elastic modulus was increased by increasing blending amount of carbon black to a level larger than that in the rubber compositions used in other rubber members of tires, a rubber composition in which elastic modulus was increased by blending a novolak type phenol resin (JP-B-57-30856), a rubber composition in which elastic modulus was increased by blending a novolak type oil-modified phenol resin with a short fiber (JP-A-6-192479), a rubber composition in which elastic modulus was increased by blending a short fiber with an olefin-based resin (JP-A-7-315014) and the like.

[0003]

[Problems that the Invention is to Solve]

In the case of the method for increasing blending amount of carbon black, the exothermic reaction when repeatedly deformed becomes large as the amount of carbon black becomes large, so that satisfactory elastic modulus cannot be obtained due to a limitation to the blending amount of carbon black. In the case of the method for blending a novolak type phenol resin, not only the phenol resin has poor compatibility with rubber generally used in tires but also, when blended in a large amount, the unreacted part remains and acts as an extraneous material, so that satisfactory elastic modulus cannot be obtained when blended in a large amount due to a limitation to its blending amount because the fatigue resistance is lowered. The short fiber blended in the rubber composition acts as an extraneous material and lowers the fatigue resistance, so that there is a limitation to its blending amount. As has been described in the above, fully satisfactory elastic modulus cannot be obtained even when the conventional methods are combined, so that concern has been directed toward a rubber composition for bead filler, which shows further high elastic modulus without spoiling physical properties such as fatigue resistance.

[0004]

Taking the above-described problems into consideration, the invention aims at providing a rubber composition having improved elastic modulus without spoiling fatigue resistance, for use in the rubber members to be arranged in the bead part of tires, particularly bead filler.

[0005]

[Means for Solving the Problems]

Through the try and error carried out in order to achieve the above-mentioned object, the following information was obtained. That is, a composition of cis-1,4-bonded polybutadiene rubber modified with a syndiotactic-1,2-bonded polybutadiene has a property of showing higher elastic modulus than that of a rubber composition in which other diene-based rubber was used and the same amount of carbon black was blended, but there is a problem in that its fatigue resistance is slightly poor. However, when the blending amount of carbon black is reduced by blending with other diene-based rubber, elastic modulus can be increased without spoiling the fatigue resistance so that the problem can be dissolved. On the other hand, when blended with rubber, resorcin or a resol type resorcin derivative obtained by allowing resorcin to react with formalin shows a higher effect to increase elastic modulus than the case of a novolak type phenol resin, so that high elastic modulus can be obtained with a small blending amount and it does not have the aforementioned problem of poor compatibility with rubber which is found when the novolak type phenol resin is blended in a large amount. In the case of a tire in which the bead filler is formed using a rubber composition wherein elastic modulus was improved by further blending resorcin or the resorcin derivative with a rubber composition prepared by blending a cis-1,4-bonded polybutadiene rubber modified with a syndiotactic-1,2-bonded polybutadiene with other diene-based rubber and also blending carbon black, its bead durability is lowered due to the aptness to generate cracks in the bead filler, but the generation of cracks can be

inhibited by blending a small amount of silica so that, as a result, the bead durability can be maintained or improved even when the elastic modulus is increased to a level higher than the conventional case.

[0006]

The invention has been accomplished based on the above-mentioned information. That is, it is a rubber composition for tire bead filler, which comprises from 3 to 20 parts by weight of silica and from 0.5 to 3 parts by weight of resorcin or a resorcin derivative, based on 100 parts by weight of a rubber component comprising from 10 to 40% by weight of a cis-1,4-bonded polybutadiene rubber modified with a syndiotactic-1,2-bonded polybutadiene and from 90 to 60% by weight of a diene-based rubber other than the cis-1,4-bonded polybutadiene rubber modified with a syndiotactic-1,2-bonded polybutadiene, wherein hexamethylenetetramine or a melamine derivative is further contained in an amount of from 0.8 to 2.0 times by weight of the blending amount of resorcin or a resorcin derivative, and storage elastic modulus (E') of its vulcanizate at a temperature of 30°C is from 8 to 15 MPa.

[0007]

[Mode for Carrying Out the Invention]

The cis-1,4-bonded polybutadiene rubber modified with a syndiotactic-1,2-bonded polybutadiene (the term "cis-1,4-bonded polybutadiene rubber modified with a syndiotactic-1,2-bonded polybutadiene" as used in the text is referred to as VCR hereinafter), which is used in the present invention, can be obtained by the method described in JP-A-55-31802, namely a method in which 1,3-butadiene is polymerized in an organic solvent in the presence of a 1,2-polymerization catalyst, and then an organic solvent solution of cis-1,4-polybutadiene rubber is added to the polymer liquid of syndiotactic-1,2-bonded polybutadiene obtained by deactivating the catalyst and mixed with stirring, and a mixture of the syndiotactic-1,2-bonded polybutadiene and cis-1,4-

bonded polybutadiene rubber is separated from the mixed liquid, or by the method described in JP-A-5-194658, namely a method in which 1,3-butadiene is firstly polymerized into cis-1,4-polybutadiene in the presence of a 1,4-polymerization catalyst without carrying out complete conversion, and then the remaining 1,3-butadiene is allowed to undergo the 1,2-polymerization by adding a 1,2-polymerization catalyst to the polymerization system. Alternatively, this can be obtained from Ube Industries, Ltd. under a trade name of UBEPOL VCR.

[0008]

As the diene-based rubber other than VCR, there is no particular limitation with the proviso that it is generally used as a rubber component of rubber compositions for tires, and natural rubber, isoprene rubber (IR), low cis-1,4-butadiene rubber, high cis-1,4-butadiene rubber and styrene·butadiene rubber (SBR) can be exemplified. Among them, natural rubber is desirable because of its small exothermic nature, high elastic modulus and large tearing strength.

[0009]

When the blending ratio of VCR which is a rubber component is lower than 10% by weight, the effect to increase elastic modulus by blending VCR does not occur, and when it becomes higher than 40% by weight, fatigue resistance is lowered and cracks are apt to be generated so that bead durability is lowered when used in the bead filler of a tire.

[0010]

The resorcin derivative to be used in the invention is a product prepared by carrying out condensation polymerization of resorcin and formalin to such a degree that the reaction can be further advanced when a methylene donor is added, and is available from SUMITOMO CHEMICAL CO., LTD. under trade names of SUMIKANOL 600 and SUMIKANOL 620. The melamine derivative is mono or polymethoxymelamine

obtained by allowing formalin to react with melamine or a mixture of both and may contain ether bond. These are available from SUMITOMO CHEMICAL CO., LTD. under trade names of SUMIKANOL 507 and SUMIKANOL 508. When blending amount of resorcin or a resorcin derivative is smaller than 0.5 part by weight (the term "part by weight" as used in the text is simply referred to as "part" hereinafter) based on 100 parts of the rubber component, the effect to increase elastic modulus to be exerted by these does not appear, and when it becomes larger than 3 parts, fatigue resistance of the vulcanizate is lowered. Blending amount of the hexamethylenetetramine or melamine derivative to be added as the methylene donor of resorcin or a resorcin derivative is set to a general blending amount and set to from 0.8 to 2.0 times by weight of the resorcin or resorcin derivative.

[0011]

When blending amount of silica is less than 3 parts based on 100 parts of the rubber component, the effect to be exerted by silica does not appear, while fatigue resistance is lowered when it becomes larger than 20 parts. It is rather desirable to avoid use of a silane coupling agent which is generally added when silica is formulated.

[0012]

In order to control storage elastic modulus of the vulcanizate at a temperature of 30°C at a level of from 8 to 15 MPa, blending amounts of VCR, silica and resorcin or a resorcin derivative are adjusted within the above-mentioned ranges or blending amount of carbon black is adjusted. When the storage elastic modulus is smaller than 8 MPa, improvement of the modulus of rubber elastic modulus cannot be attained, and when it becomes larger than 1.5 MPa, fatigue resistance is lowered so that bead durability is lowered when used in the bead filer of a tire.

[0013]

In addition to the aforementioned silica, resorcin or resorcin derivative and hexamethylenetetramine or melamine derivative, various compounding agents generally blended in rubber compositions for tires can be optionally blended with the rubber composition of the invention, and their blending amounts can also be set to the general amounts. As the compounding agents to be optionally blended, for example, carbon black, sulfur, a vulcanization accelerator, zinc flower and the like can be mentioned.

[0014]

[Examples]

The respective rubber components shown in Table 1 or Table 2 were blended with carbon black and silica at respective part by weight ratios shown in Table 1 or Table 2, further blended with 3 parts of zinc flower, 1 part of stearic acid, 2 parts of oil and 1 part of an antioxidant (trade name NOCRAC 6C, manufactured by OUCHI SHINKO CHEMICAL INDUSTRIAL Co., Ltd.), followed by mixing using Banbury mixer in accordance with a general method. They were discharged once and cooled, followed by further mixing with resorcin in respective amounts shown in Table 1 or Table 2. Then, they are discharged and cooled, followed by further mixing with hexamethylenetetramine in respective amounts shown in Table 1 or Table 2 and 2 parts of sulfur and 1 part of a vulcanization accelerator CBS, thereby obtaining respective mixed rubbers.

[0015]

By taking out a sample from each of the above-mentioned mixed rubbers, storage elastic modulus was measured by the method described in the following. The results are shown in Table 1 or Table 2.

[0016]

In addition, a tire of 11R22.5 in size was produced as an experiment using each of the above-mentioned mixed rubbers in the bead filler. A durability test was carried

out on each of the prototype tires by the method described in the following. The results are shown in Table 1 or Table 2.

[0017]

[Table 1]

	Examples								
Prototype No.	1	2	3	4	5	6	7	8	9
Natural rubber	90	80	70	60	80	80	80	80	80
VCR	10	20	30	40	20	20	20	20	20
Carbon black N330	45	45	45	45	50	40	45	45	45
Silica	10	10	10	10	3	20	10	10	10
Resorcin	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.5	3.0
Hexamethylenetetramine	0.8	0.8	0.8	0.8	0.8	0.8	2.0	0.4	2.4
Storage elastic modulus (MPa)	10.0	10.1	10.3	12.3	11.5	8.8	10.6	8.0	14.9
Durability	○	○	○	○	○	○	○	○	○

[0018]

[Table 2]

	Comparative Examples							
Prototype No.	C1	C2	C3	C4	C5	C6	C7	C8
Natural rubber	100	50	80	80	80	80	80	80
VCR	-	50	20	20	20	20	20	20
Carbon black N330	45	45	50	30	45	45	45	35
Silica	10	10	-	30	10	10	10	10
Resorcin	1.0	1.0	1.0	1.0	1.0	1.0	-	5.0
Hexamethylenetetramine	0.8	0.8	0.8	0.8	0.5	3.0	-	4.0
Storage elastic modulus (MPa)	9.6	12.6	11.7	7.2	9.2	10.9	6.0	16.1
Durability	△	×	△	△	△	△	×	△

[0019]

Storage elastic modulus: Each mixed rubber was put into a mold and vulcanized at 150°C for 30 minutes to produce a specimen, and this was measured using a visco-elastic modulus spectrometer manufactured by Iwamoto Seisakusho under

conditions of 30°C in temperature, 15% in extension ratio, 1% in amplitude and 50 Hz in frequency.

Durability: Each prototype tire was rimmed, filled with air of 0.9 MPa in internal pressure, set on a drum tester and subjected to drum traveling with a load of 5,400 kg and at a velocity of 40 km/hr until a failure is generated, and the traveled period of time was regarded as the durability. A result in which the durability was improved by 10% or more than the case of Comparative Example C1 was rated as ○, and the improvement of less than ± 10% as △, and that of lowering by 10% or more as ×. In this connection, since the above-mentioned load was set to about 2 times of the design load, the failure was generated at the bead part.

[0020]

Though the bead fillers of the prototype tires other than those of Examples 6 and 8 were formed using rubber compositions having higher elastic modulus than that of Comparative Example C1, their durability were improved by 10% or more than the case of Comparative Example C1. On the other hand, when Examples 1, 2, 3 and 4 and Comparative Example C2 having the same blending amounts of the compounding agents are respectively compared, it can be seen that elastic modulus is increased as the blending ratio of VCR is increased and the durability is lowered when the blending ratio of VCR becomes higher than 40% by weight. In addition, comparison of Example 5 and Comparative Example C3 shows that silica has the action to improve durability, but comparison of Examples 1, 5 and 6 and Comparative Examples C3 and C4 shows that the durability improving effect is not exerted when the blending amount of silica becomes larger than 20 parts. Improvement of durability is not observed in Comparative Examples C5, C6, C7 and C8 in which blending amounts of one or both of resorcin and hexamethylenetetramine are outside of the specified ranges.

[0021]

[Advantage of the Invention]

By making a rubber composition to be used in bead fillers into a composition in which, in the rubber component, VCR is contained in an amount of from 10 to 40% by weight, from 3 to 20 parts of silica and from 0.5 to 3 parts of resorcin or a resorcin derivative are blended based on 100 parts of the rubber component, and hexamethylenetetramine or a melamine derivative is contained in an amount of from 0.8 to 2.0 times by weight of the blending amount of resorcin or resorcin derivative, its elastic modulus is increased and bead durability of a tire is improved when it is used in the bead filler.